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XXII.

CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF HARVARD COLLEGE.

ON THE ACTION OF SODIUM ACETACETIC ESTER UPON TRIBROMDINITROBENZOL.

By C. Loring Jackson and George Dunning Moore.

Presented May 28, 1889.

After the action of sodium malonic ester on tribromtrinitrobenzol and on tribromdinitrobenzol had been studied, it seemed of interest to determine whether sodium acetacetic ester acted in the same way, and the following paper contains the results of experiments undertaken with this intention upon the tribromdinitrobenzol, which was selected, because it can be prepared so much more easily than the corresponding trinitro compound. These results can be summarized briefly as follows. Tribromdinitrobenzol behaves with sodium acetacetic ester in the same way that it does with sodium malonic ester; that is, one atom of its bromine is replaced by the acetacetic radical

$$CH_3COCHCOOC_2H_5,$$

and a second by hydrogen, while the third remains unaltered; so that the product of the action is the bromdinitrophenylacetacetic ester,

$$C_6H_2Br(NO_2)_2CH_3COCHCOOC_2H_5,$$

or to speak more accurately its sodium salt,

$$C_6H_2Br(NO_2)_2CH_3COCNaCOOC_2H_5,$$

The bromdinitrophenylacetacetic ester melts at 96°, and possesses marked acid properties, forming the sodium salt whose formula has just been given, even with acid sodic carbonate in aqueous solution. The salt has a red color, and is soluble in water; in fact, it resembles the sodium salt of the corresponding malonic compound most closely.

The bromdinitrophenylacetacetic ester is saponified and decomposed by heating with sulphuric acid of specific gravity 1.44, giving the bromdinitrobenzylmethylketone,

$$C_6H_2Br(NO_2)_2CH_2COCH_3,$$

but no trace of the corresponding acetic acid. This ketone melts at 112°–113°, and also possesses acid properties, giving a purplish red salt soluble in alcohol, but decomposed almost completely by water. The acid properties of the ketone are less marked than those of the acetacetic ester, as was to be expected, since the hydrogen, which is replaced by basic radicals, is subject to the influence of an acetyl, a carboxylester, and a dinitro phenyl group in the acetacetic compound, only to those of an acetyl and a dinitro phenyl group in the ketone.

The bromine of the ketone can be replaced easily by the aniline radical C_6H_5NH, forming anilidodinitrobenzylmethylketone,

$$C_6H_2(C_6H_5NH)(NO_2)_2CH_2COCH_3,$$

which melts at 131°, and has not lost all acid properties, although they have been much weakened by replacing the bromine atom by the basic radical C_6H_5NH. It cannot form an ammonium salt, but the sodium salt can be easily obtained in alcoholic solution, and on analysis gave a number corresponding to the formula

$$C_6H_2(C_6H_5NH)(NO_2)_2CHNaCOCH_3.$$

It is completely decomposed by water, but dissolves in alcohol with a brown color.

Both these ketones, therefore, show stronger acid properties than desoxybenzoine $C_6H_5COCH_2C_6H_5$, the metallic compounds of which, according to Victor Meyer,* could not be isolated; we are inclined to ascribe this to the presence of the nitro groups in the phenyl, which would heighten its acid-producing power, but it may also be due in part to the fact that these ketones contain the acetyl group, which, as Claisen and Ehrhardt † have pointed out, has a greater influence in producing acidity than the benzoyl radical contained in desoxybenzoine.

The hydrazone of the anilidodinitrobenzylmethylketone,

$$C_6H_2(C_6H_5NH)(NO_2)_2CH_2C(NNHC_6H_5)CH_3,$$

was also prepared, and melted at 140°.

The full details of the work will be found in the remainder of the paper.

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* Ber. d. ch. G. 1888, p. 1291.

† Ber. d. ch. G. 1889, p. 1019.

Preparation of Tribromdinitrobenzol.

The method used by us for preparing tribromdinitrobenzol differs from that formerly in use only in certain details, but, as careful attention to these details insures a purer product at much less expense of time and labor, we have thought it best to give a full account of our mode of procedure.

To make the tribromaniline, 60 grs. of aniline were dissolved in dilute hydrochloric acid, and, the solution having been made up to a volume of about 3 litres, a rapid stream of air saturated with bromine vapor was sucked through it by means of a Bunsen pump, until the liquid assumed a distinct yellow color. The precipitate of tribromaniline was then removed by straining through cheese-cloth, and washed with a stream of common water, until free from acid, when the greater part of the water was squeezed out with a screw press, and the product thoroughly dried on a steam radiator. In this way a quantitative yield of the tribromaniline was obtained, and it was free from colored by-products.

In order to convert the tribromaniline into tribrombenzol, 50 grs. of it, after being pulverized, were dissolved with the aid of heat in about 300 c.c. of common alcohol, and a concentrated aqueous solution of 21 grs. of sodic nitrite poured in slowly, but not in successive portions. The hot mixture was then acidified with dilute sulphuric acid, and allowed to stand over night, when it was filtered, and the precipitate washed with hot water to remove the sodic sulphate and leave the tribrombenzol. An additional quantity of this was obtained by concentrating the alcoholic filtrate, when it separated as an oil, that solidified on standing, and was then crystallized from alcohol. The yield was nearly quantitative, as 45.50 grs. of tribrombenzol were obtained instead of the 47.77 required by the theory, that is 95 per cent. When made by this method, the tribrombenzol was usually pure enough to be nitrired directly in spite of its brownish color.*

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* The amount of sodic nitrite used in the process described above (two molecules of nitrite to one of the base) is twice that required by the theory, but we have found that this large excess was necessary to bring all the tribromaniline into the reaction. When a smaller amount of nitrite was used, the product was much less pure, as shown by its lower melting point; it was necessary in this case to distil it from a little retort, and crystallize several times from alcohol, to obtain pure tribrombenzol. The crystals obtained on evaporating the alcoholic mother liquors, which made up about two thirds of the entire amount, were distilled with steam, pushing the distillation as rapidly as possible, when tribrombenzol passed over, and tribromaniline was left in the retort; but all this tedious purification can be avoided by using the excess of nitrite recommended above.

To convert the tribrombenzol into the dinitro compound, 25 grs. of it were added to 100–120 grs. of nitric acid* of specific gravity 1.52, (made from potassic nitrate and sulphuric acid in the laboratory,) warmed gently until the solid had dissolved, and allowed to stand about two hours, when the tribromdinitrobenzol crystallized out in large white prisms. The yield was essentially quantitative.

Bromdinitrophenylacetacetic Ester,
$C_6H_2Br(NO_2)_2CH_3COCHCOOC_2H_5$.

Preparation. — This substance was made by the action of an alcoholic solution of sodium acetacetic ester on a benzol solution of the tribromdinitrobenzol in the proportion of about four molecules of the former to one of the latter. For this purpose 15 grs. of tribromdinitrobenzol were dissolved in about 200 c.c. of benzol, and mixed with 20 grs. of acetacetic ester previously treated with 3 grs. of sodium dissolved in about 20 c.c. of absolute alcohol. At first there was very little change of color, but on standing at ordinary temperatures the liquid turned first yellow and then red (whereas with malonic ester the red color appeared instantaneously). In order to complete the reaction, the mixture was heated on the steam bath for about one hour, at the end of which time it had become nearly black, and a considerable precipitate of sodic bromide had formed. It was then mixed with from one and a half to two litres of water, and the reddish benzol solution, which was precipitated, removed from the dark red aqueous liquid; the latter was then acidified with dilute sulphuric acid, taking care to avoid a large excess; this decomposed the red sodium salt of the new substance, which was set free in the form of a yellowish oil, and extracted by shaking the liquid with ether twice. On distilling off the ether a dark reddish brown oil was left, which, when cold, was treated with very little alcohol, and upon stirring became filled with crystals, the quantity of which increased on standing for twelve or more hours. When the quantity of the crystals did not increase further, the pasty mass was sucked out on the pump, first adding a little alcohol, if necessary, and by washing with a small quantity of cold alcohol all the very soluble red oil was removed from the crystals, which were nearly or quite insoluble in cold alcohol, and were next purified by crystallization from hot alcohol until they showed the constant melting point 96°. An additional quantity of the substance can be obtained from the benzol solution by distilling off the benzol and treating the residue with sodic hydrate and a little alcohol, which convert the new substance into its sodium salt, and this can be removed from the unaltered tribromdinitrobenzol by washing with water; when the wash-waters were acidified, and the precipitate purified in the same way as the main portion, the substance was dried *in vacuo*, and analyzed with the following results: —

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* These Proceedings, xxii. 374.

I. 0.2683 gr. of the substance gave on combustion 0.3788 gr. of carbonic dioxide, and 0.0748 gr. of water.

II. 0.2512 gr. of the substance gave 16.7 c.c. of nitrogen at a temperature of 22° and a pressure of 759.7 mm.

III. 0.2067 gr. of the substance gave, according to the method of Carius, 0.1041 gr. of argentic bromide.

IV. 0.2141 gr. of the substance gave 0.1059 gr. of argentic bromide.

	Calculated for	Found.			
	$C_6H_2Br(NO_2)_2CH_3COCHCO_2C_2H_5$.	I.	II.	III.	IV.
Carbon	38.41	38.50			
Hydrogen	2.93	3.09			
Nitrogen	7.47		7.33		
Bromine	21.33			21.43	21.05

The yield of bromdinitrophenylacetacetic ester, prepared by the method described above, is satisfactory on the whole, the best result being as follows: —

15 grs. of the tribromdinitrobenzol yielded 6.5 grs. of the ester, and 3.1 grs. of unaltered tribromdinitrobenzol were recovered, leaving 11.9 grs. which had entered into the reaction. 11.9 grs. of tribromdinitrobenzol should yield 11.0 grs. of bromdinitrophenylacetacetic ester. The actual yield, therefore, was 59 per cent of the theoretical. In other preparations the yield varied from 54 to 34 per cent, the lowest which was obtained from this process. The yield was not improved by increasing or by diminishing the proportion of acetacetic ester to the tribromdinitrobenzol. In our first preparations the reaction was allowed to run in the cold, as an experiment, in which the mixture had been heated less than one hour, seemed to give a very unmanageable product; in this case, however, the yield was very much less than that obtained by the process described above, in which the mixture was heated one hour.

In order to throw light on the way in which the reaction runs, we determined the amount of bromide of sodium formed in two preparations as follows: —

I. 12 grs. of tribromdinitrobenzol yielded 4.43 grs. of bromine in the form of sodic bromide.

II. 12 grs. of tribromdinitrobenzol yielded 4.40 grs. of bromine in the form of sodic bromide.

If two atoms of bromine are removed from each molecule by this reaction, 12 grs. of tribromdinitrobenzol would lose 4.74 grs. of bromine.

Percentage of bromine removed as sodic bromide, —

I.	II.
93.5	93.0

From this it appears that all the bromine removed from the tribromdinitrobenzol is finally in the state of sodic bromide, as the slight loss of 7 to 6.5 per cent is not greater than would be expected when it is considered that the aqueous solution containing the sodic bromide was shaken out twice with ether. These determinations show also that in these cases the whole of the tribromdinitrobenzol entered into the reaction, and in fact none of it could be found unaltered in the products of these two preparations; but this was not always the case, as, for instance, in the preparation described on page 275.

The full explanation of the reaction, however, was to be found in the study of its secondary product, the red oil removed from the crystals by washing with cold alcohol. This, upon long standing exposed to the air, threw down a few more crystals of bromdinitrophenylacetacetic ester, which would raise the yield a little above that given, but the amount obtained in this way was very small. The oil, after no more crystals could be obtained from it, was distilled under diminished pressure and yielded some acetacetic ester, leaving in the flask a tarry mass which has shown no signs of giving crystals even after long standing. This part of the work therefore was not carried further, as from the formula of the ester and the removal of all the bromine as sodic bromide there can be no doubt that the reaction with acetacetic ester runs in the same way as that with malonic ester, and in this latter case the reaction has been fully explained.* Reasoning on this analogy, the following reactions may be taken as expressing what takes place in the formation of the bromdinitrophenylacetacetic ester.

$$
\begin{aligned}
&C_6HBr_3(NO_2)_2 + 2\,CH_3COCHNaCOOC_2H_5 = \\
&\quad C_6HBr_2(NO_2)_2CH_3COCHCOOC_2H_5 + NaBr \\
&\qquad\qquad + CH_3COCHNaCOOC_2H_5 = \\
&\quad C_6HBr_2(NO_2)_2CH_3COCNaCOOC_2H_5 + CH_3COCH_2COOC_2H_5 \\
&\qquad\qquad + NaBr = \\
&\quad C_6H_2Br(NO_2)_2CH_3COCNaCOOC_2H_5 + CH_3COCHBrCOOC_2H_5 \\
&\qquad\qquad + NaBr.
\end{aligned}
$$

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* These Proceedings, xxiv. 238, 265.

The bromacetacetic ester being afterward attacked either by a molecule of sodium acetacetic ester or by sodic hydrate.

The only question with regard to these reactions, which might arise would be due to the fact that only a little over 50 per cent (59 per cent) of the ester was obtained, which might lead to the hypothesis that nearly half of the tribromdinitrobenzol went to form another substance; but this objection is removed by the fact that in another analogous case as much as 80 per cent of a corresponding ester has been found. We consider, therefore, that the missing 41 per cent of the ester remained dissolved in the oily secondary product, but should state, on the other hand, that upon treating the oil with sulphuric acid of specific gravity 1.44 in hopes of decomposing the secondary products and converting the bromdinitrophenylacetacetic ester into bromdinitrobenzylmethylketone, we obtained nothing but black tarry substances, from which no substance fit for analysis could be obtained.

Properties. — The bromdinitrophenylacetacetic ester crystallizes well, usually in forms looking like a rhombohedron with a very acute angle, less frequently in prismatic forms, which are twinned on a central line parallel to their longer axis, the termination being in shape either like a simple gable, or one with a notch in its point. The crystals show a great tendency to twin, or group, often in forms like those of frost, and are sometimes from 2 to 3 mm. long. The substance has a yellow color of about the shade of potassic chromate, which is characteristic, as the corresponding malonic compound is nearly white. Heckmann * has observed a similar deep yellow color in the orthoparadinitrophenylacetacetic ester. It melts at 96° ; is very slightly soluble in water, rather more so in hot than in cold; essentially insoluble in ligroine; not very soluble in cold alcohol, but freely in hot; if anything less soluble in methyl than in common alcohol both cold and hot, but the solubility is much greater in the hot methyl alcohol than in the same solvent when cold; tolerably soluble in carbonic disulphide, or ether; soluble in glacial acetic acid; and freely in benzol, chloroform, or acetone; from ether, benzol, or chloroform it is deposited as an oil. The best solvent for it is hot alcohol. Strong sulphuric acid does not act upon it in the cold, but when warm dissolves it, forming a slightly yellowish solution. Strong hydrochloric acid has no action with it in open vessels, even if heated. The decomposition of the substance by these two acids under proper conditions is described later in this paper. Strong nitric acid has no action on it in the cold, but dissolves it when warm; there is, however, no marked change of color in which respect this substance shows a striking difference from the bromtrinitrophenylmalonic ester, but resembles the bromdinitrophenylmalonic ester.

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* Ann. Chem., ccxx. 133.

The bromdinitrophenylacetacetic ester shows marked acid properties, as was to be expected from the position of one of its hydrogen atoms upon a carbon adjacent to an acetyl, a carboxylester, and a phenyl group, the latter rendered still more efficient by the presence of two nitro groups, and also from the acid properties of the corresponding malonic compound. Aqueous sodic, or ammonic hydrate dissolves it forming a red solution of the corresponding salt; an aqueous solution of potassic carbonate acts upon it in the same way giving, however, a somewhat fainter color, but, if alcohol is added to the solution, it turns at once dark red; acid sodic carbonate in aqueous solution gives a very faint red color which is much intensified by addition of alcohol to the solution. The red solution of the ester in ammonic hydrate is decomposed by heating, or even by exposure to the air at ordinary temperatures, and we were not able to obtain a solution, which did not smell of ammonia, even when a large excess of the ester was used, it is evident therefore that its ammonium salt is very unstable. We have, however, tried the action of a solution prepared from an excess of the ester and ammonic hydrate with various reagents, and found the following characteristic reactions.

Magnesium or Calcium salt, heavy flocculent precipitate of the color of chrome yellow.

Strontium salt, a less heavy precipitate of a redder color.

Barium salt, a still smaller precipitate, also reddish.

Zinc salt, a pale yellow precipitate.

Cupric salt, a pale yellow precipitate.

Lead salt, a dark yellow precipitate.

Silver salt, a yellowish white precipitate.

The most striking thing about these salts is that the calcium salt is less soluble than that of strontium, and this less soluble than the barium salt. Bischoff* has observed a similar peculiarity in the salts of orthonitrobenzoylmalonic ester, and we have found it in the salts of bromtrinitrophenylmalonic ester.

With aniline the bromdinitrophenylacetacetic ester gave only a waxy yellow mass, from which there seemed little chance of obtaining a substance in a state fit for analysis. We have, therefore, abandoned the further study of this reaction, in which undoubtedly the aniline acted on the acetacetic ester radical as well as on the bromine in the benzol ring. That this bromine had been removed we proved by detecting aniline bromide among the products of the reaction.

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* Ann. Chem., ccli. 362.

Sodium Salt, $C_6H_2Br(NO_2)_2CH_3COCNaCOOC_2H_5$.

In the earlier portions of our work on the bromdinitrophenylacetacetic ester and allied bodies the determination of the composition of the salts was of the greatest importance, as this was the only experimental method which we had found for deciding between the formulas,

I. $C_6H_2Br(NO_2)_2CH_3COCHCOOC_2H_5$,
II. $C_6HBr(NO_2)_2CH_3COCCOOC_2H_5$.

This, at present, is no longer the case, as the discovery of acetylentetracarbonic ester or tartronic acid as a secondary product in the formation of the corresponding malonic compounds can be explained only if a formula similar to I. is adopted, and the easy conversion of bromdi- (or tri-) nitrophenylmalonic ester into the corresponding toluol compound also could hardly be brought into harmony with a formula like II. No similar proof has been applied to the acetacetic compound, it is true; but when the close resemblance between this and the malonic compounds is considered, there can be no doubt that they are similarly constituted. The composition of the sodium salt therefore becomes of secondary importance, and this is fortunate, as we have not succeeded in preparing it in a state of purity sufficient to decide between the salts derived from formulas I. and II., although our analyses leave no doubt as to its composition, if the first formula is adopted as correct.

The salt was prepared by adding to a solution of the bromdinitrophenylacetacetic ester in absolute alcohol a solution of sodic hydrate or ethylate also in absolute alcohol, taking care that the ester was in decided excess. The deep red alcoholic solution thus obtained was evaporated rapidly to dryness in a narrow beaker sunk throughout its whole height in a water bath, some ether having been added previously in order that its vapor might protect the solution from the carbonic dioxide of the air until the alcohol began to boil. The excess of ester was washed out of the dry residue with benzol, and the salt dried at 100°, and analyzed with the following results: —

I. 0.2102 gr. of the salt gave after treatment with sulphuric acid 0.0361 gr. of sodic sulphate.

II. 0.2056 gr. of the salt gave 0.0407 gr. of sodic sulphate.
III. 0.2531 gr. of the salt gave 0.0390 gr. of sodic sulphate.

	Calculated for	Found.		
	$C_6H_2Br(NO_2)_2CH_3COCNaCO_2C_2H_5$.	I.	II.	III.
Sodium	5.79	5.56	6.41	4.99

It is evident from these results that the method of preparation is unsatisfactory, and we ascribe this to the action of the sodic hydrate (or ethylate) on the bromine, and perhaps also on the acetacetic radical, as, when these two sources of error were removed by using the anilidodinitrobenzylmethylketone, an excellent result was obtained. Bad as these analytical results are, they show that the salt contains but one atom of sodium, and therefore must have the formula which we have ascribed to it.

Properties. — The sodium salt of the bromdinitrophenylacetacetic ester forms a brick-red amorphous mass, easily soluble in water, alcohol, or ether, but insoluble in benzol. Much less freely soluble in a solution of sodic hydrate than in water. Strong nitric acid decomposes it, giving apparently the unaltered ester.

Bromdinitrobenzylmethylketone (*Bromdinitrophenylacetone*), $C_6H_2Br(NO_2)_2CH_2COCH_3$.

This substance can be made from the bromdinitrophenylacetacetic ester by the action of dilute sulphuric acid in open vessels, or of strong hydrochloric acid in sealed tubes. The method of preparation which gave us the best results was as follows: 2 to 2.5 grs. of bromdinitrophenylacetacetic ester were boiled with about 200 c.c. of sulphuric acid of specific gravity 1.44, boiling point 132°, in a flask with a return condenser, until all the solid was dissolved, which took usually from one hour to an hour and a half. The yellow solution was then allowed to cool, when it deposited a heavy white flocculent precipitate, which was increased in quantity by diluting largely with water; it was filtered out, and after thorough washing with water was purified by crystallization from alcohol until it showed the constant melting point 112°–113°, when it was dried at 100° for analysis. If the ester used in this process was not perfectly pure, a tarry impurity was formed which could be removed only with great difficulty; the best plan in such a case was to wash the product with a small quantity (20–30 c.c.) of benzol, which dissolved the ketone more readily than its impurity, but even after this treatment tedious crystallization from alcohol was necessary to obtain a pure substance.

The formation of this substance by heating the bromdinitrophenylacetacetic ester with hydrochloric acid is not a good method of preparing it, because the process must be carried on in sealed tubes, and also because the product is apt to be contaminated with the tarry impurity just mentioned; but as it throws light on the reaction which takes place, we will describe it briefly: 1 gr. to 1.5 grs. of the ester were sealed in a tube with 20–30 c.c. of pure strong hydrochloric acid, and heated from 130°–150° for two or three hours. Upon opening the tube a gas was evolved, which burnt with a smoky green-bordered flame (ethylchloride), and also contained carbonic dioxide, as shown by its giving a precipitate with lime-water. The contents of the tubes consisting, in addition to the acid liquid, either of tufts of brownish acicular crystals, or a brown oily semi-solid mass, were poured into a large volume of cold water, and the insoluble portions purified as already described.

The following analyses were made in part with substance prepared by the hydrochloric acid process, and in part with that made with sulphuric acid: —

I. 0.2312 gr. of the substance gave on combustion 0.3005 gr. of carbonic dioxide, and 0.0546 gr. of water.

II. 0.1638 gr. of the substance gave 14 c.c. of nitrogen at a temperature of 23° and a pressure of 755 mm.

III. 0.1862 gr. of the substance gave, according to the method of Carius, 0.1173 gr. of argentic bromide.

	Calculated for $C_6H_2Br(NO_2)_2CH_2COCH_3$.	Found.		
		I.	II.	III.
Carbon	35.64	35.44		
Hydrogen	2.31	2.62		
Nitrogen	9.24		9.57	
Bromine	26.40			26.81

It is evident from the analyses and observations given above that the reaction with hydrochloric acid runs as follows: —

$$C_6H_2Br(NO_2)_2CH_3COCHCO_2C_2H_5 + HCl = C_2H_5Cl + CO_2 + C_6H_2Br(NO_2)_2CH_2COCH_3;$$

and that the reaction with sulphuric acid must be similar. We had expected that bromdinitrophenylacetic acid would be formed also by these processes, but after a most careful search for it not a trace could be detected; and as its properties are so striking that we could not have overlooked it, the conclusion is forced upon us that the reaction consisted only in the formation of the ketone. This result is the more remarkable because Heckmann[*] obtained from the orthoparadinitrophenylacetacetic ester by treatment with sulphuric acid of about 10 per cent exclusively the dinitrophenylacetic acid without a trace of the corresponding ketone. As the presence of bromine in our compound could hardly have caused such a great difference in the action of the sulphuric acid, we infer that it must have been caused by the difference in strength of the sulphuric acid, Heckmann's containing about 10 per cent of H_2SO_4, while ours contained 54 per cent. This inference will be tested by experiment in the coming year.

Properties. — The bromdinitrobenzylmethylketone crystallizes from hot alcohol by cooling in white rectangular plates, often with a right-angled notch in one corner, sometimes also in plates with parallel sides and a deep notch in each end, which makes them look like reels. If crystallized by the evaporation of its alcoholic solution, it forms cylindrical tufts of needles looking like spires of moss, or much branched forms resembling certain seaweeds. Both the plates and the branching needles commonly occur together. It melts at 112°–113° and is essentially insoluble in ligroine; nearly insoluble in cold water, more soluble in hot, but still very sparingly; slightly soluble in ether, carbonic disulphide, benzol, or methyl alcohol, its solubility in the last two solvents is increased by heat; tolerably soluble in ethyl alcohol in the cold, freely when hot; ethyl alcohol dissolves it more freely than methyl alcohol; tolerably soluble in glacial acetic acid; soluble in chloroform; and freely soluble in acetone. Hot alcohol is the best solvent for it. Strong sulphuric acid has no action on it in the cold, but when warmed dissolves it, forming a colorless solution from which water precipitates the ketone essentially unaltered, although it appears at first in spherical groups of thickly set radiating needles, a form in which it is also obtained sometimes when prepared by the action of sulphuric acid on bromdinitrophenylacetacetic ester, but these crystals are converted by crystallization from alcohol into the rectangular plates described above. Strong nitric acid acts like strong sulphuric acid.

The bromdinitrobenzylmethylketone has well marked acid properties, and in this respect far surpasses the desoxybenzoine from which according to Victor Meyer[†] no sodium compound could be isolated. In alcoholic solution the ketone gives a dark purplish red color with sodic hydrate or ethylate. Aqueous ammonic hydrate gives only a slight red color with it, which is increased by warming for a short time, and still more by the addition of alcohol, but the color disappears if the heating is long continued. Aqueous potassic carbonate gave no action, but on the addition of alcohol a very dark purplish red solution of the salt. Acid sodic carbonate had no action in aqueous solution, and only very slight on addition of alcohol. The dark red alcoholic solution of the ammonium or sodium salt, if made with an excess of the ketone, is decomposed by water, giving a white precipitate of the ketone. The decomposition is not complete, however, as the liquid retains a pale red color. In the presence of an excess of sodic hydrate, the salt is much more stable. An attempt was made to study the action of the pale red aqueous solution of the ammonium salt with various reagents, but no characteristic precipitates were obtained, probably on account of the small amount of salt left in solution.

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[*] Ann. Chem., ccxx 134.

[†] Ber. d. ch. G. 1888, p. 1291.

We tried also to prepare and analyze the sodium salt, the method being that adopted for the sodium salt of the bromdinitrophenylacetacetic ester; but the results of the analyses came much too high, 9.73 and 8.64 per cent of sodium, instead of the 7.07 per cent required by the formula. The reason for this difference is that the sodic hydrate or ethylate removed a portion of the bromine from the ketone, and the benzol, dissolving the organic product, left the sodic bromide formed with the salt of the ketone, as was proved by dissolving the salt in water, and acidifying with nitric acid, when, after removing the precipitate by filtration, argentic nitrate gave a heavy precipitate of argentic bromide in the filtrate. We accordingly turned our attention to the anilidoketone, our work on which is described later in this paper. We add here the *properties* of the *sodium salt of bromdinitrobenzylmethylketone.* It is a purplish black amorphous substance, very easily soluble in alcohol forming a dark claret-red solution, the color of which is so much more purple than that of the salt of the corresponding acetacetic ester, that the two substances can be easily distinguished in this way ; it is decomposed almost, but not quite, completely by water, and is insoluble in benzol.

The ketone is a decidedly reactive substance. When treated with aniline, it gives aniline bromide and the anilidodinitrobenzylmethylketone, which is described later. With phenylhydrazine it appears to form a hydrazone, but at the same time the bromine was removed from the benzol ring, so that the product seemed to be a phenylhydrazidohydrazone. It was free from bromine, and exploded when touched with a hot wire; but as its purification offered considerable difficulties, we did not try to investigate it thoroughly. The ketone seems to react in the same way with hydroxylamine, since in this case also bromine seemed to be removed; but as the product did not have inviting properties, we have not attempted to isolate the oxime. If the ketone is dissolved in chloroform, the solution mixed with bromine, and allowed to stand at ordinary temperatures, hydrobromic acid is given off in considerable quantity, and a new substance melting at least 10° higher than the original is formed, which will be investigated in this laboratory next term. It is a curious fact, that, if a solution of the ketone in carbonic disulphide instead of chloroform was treated with bromine, no hydrobromic acid was given off, so far as we could find.

Anilidodinitrobenzylmethylketone, $C_6H_2(C_6H_5NH)(NO_2)_2CH_2COCH_3$.

This substance is prepared easily by the action of aniline on the bromdinitrobenzylmethylketone. The substances were mixed in the proportion of one molecule of the ketone to two of the base, and the mixture, which had a bright red color, warmed for 15 to 20 minutes on the water bath. The product was then freed from the aniline bromide and any slight excess of aniline by washing with water to which a little hydrochloric acid was added, the residue, which contained no bromine, purified by crystallization from hot alcohol till it showed the constant melting point 131°, dried at 100°, and analyzed with the following result: —

0.1980 gr. of the substance gave 23.2 c.c. of nitrogen at a temperature of 25° and a pressure of 771.2 mm.

	Calculated for $C_6H_2C_6H_5NH(NO_2)_2CH_2COCH_3$.	Found.
Nitrogen	13.33	13.26

Properties. — The anilidodinitrobenzylmethylketone forms, when crystallized from alcohol, bright yellow groups of curving needles, which look at first like two heads of palm trees cut off at the point where the leaves grow out of the trunks, and put with the stumps together. As more crystals are formed, the groups develop into irregular chestnut burs. It melts at 131°; is essentially insoluble in ligroine; nearly insoluble in cold water, slightly soluble in hot, forming a pale yellow solution; slightly soluble in ether; soluble in cold ethyl or methyl alcohol, more freely in either of these solvents when hot; soluble in benzol, carbonic disulphide, or glacial acetic acid; freely soluble in chloroform or acetone. Alcohol is the best solvent for obtaining crystals. Strong sulphuric acid dissolves it, forming a brown solution. Strong nitric or hydrochloric acid dissolves it with a yellow color, but it is very slightly soluble in hydrochloric acid.

The acid properties of this substance are much less marked than those of the corresponding bromine compound, as was to be expected from the substitution of bromine by the basic radical C_6H_5NH. Aqueous sodic hydrate has no action on it in the cold, and but slight when warm, but if alcohol is added a brownish red solution of the sodium salt is obtained. Ammonic hydrate, on the other hand, could not be made to act on it, even by warming in presence of a large excess of alcohol. Potassic carbonate in aqueous solution had no action on it, either cold or hot, but gave a very slight action when a large quantity of alcohol was added. The behavior of the solution of a soluble salt with various reagents could not be studied, as the alcoholic solution of the sodium salt was decomposed completely by diluting it with water. But in spite of these weaker acid properties we selected the sodium salt of this substance for analysis, as there was no danger of a decomposition of this ketone by the alkali used, such as had prevented us from getting good results with the corresponding bromine compound. For the same reason, the hydrazone for analysis was prepared from this substance instead of from the bromdinitrobenzylmethylketone.

Sodium Salt of Anilidodinitrobenzylmethylketone, $C_6H_2(C_6H_5NH)(NO_2)_2CHNaCOCH_3$.

This substance was prepared by adding an alcoholic solution of sodic ethylate to an excess of the ketone also dissolved in absolute alcohol. The narrow beaker containing the mixture, after the addition of a little ether, was sunk to its rim in a steam bath. In this way, at first the ether, and later the alcohol vapor, prevented the carbonic dioxide of the air from acting on the salt during the evaporation. The dry residue was thoroughly washed with benzol to remove the excess of the ketone, and the salt thus purified dried at 100°, and analyzed with the following result: —

0.2380 gr. of the salt gave after evaporation with sulphuric acid 0.0500 gr. of sodic sulphate.

	Calculated for $C_6H_2(C_6H_5NH)(NO_2)_2C_3OH_4Na$.	Found.
Sodium	6.82	6.80

Properties. — A brownish black mass, soluble in alcohol, giving a much browner solution than any of the other salts described in this paper, so that it could be recognized with ease by its color. It is decomposed at once by water, the brown alcoholic solution being turned yellow and turbid. It seems to be nearly or quite insoluble in ether, and is insoluble in benzol.

Anilidodinitrobenzylmethylketonehydrazone, $C_6H_2(C_6H_5NH)(NO_2)_2CH_2C(N_2HC_6H_5)CH_3$.

This substance was made by warming for 20–30 minutes on the water bath in an open dish a mixture of anilidodinitrobenzylmethylketone with phenylhydrazine in the proportion of one molecule of the former to about one and a half of the latter, so as to have a decided excess of the hydrazine. At the end of this time the mixture had changed from yellow to dark carmine red, and solidified to a tarry mass, which was crystallized once or twice from alcohol to bring it into a finely divided state, and washed with water containing a little hydrochloric acid till the excess of phenylhydrazine had been removed, after which it was boiled with alcohol on the water bath, and while boiling enough benzol added cautiously to effect the solution; the mixture was then boiled for about a minute, when upon cooling crystals were deposited, and this crystallization was continued until the substance showed the constant melting point 140°, when it was dried at 100°, and analyzed with the following result: —

0.2177 gr. of the substance gave 32.5 c.c. of nitrogen at a temperature of 22° and a pressure of 763 mm.

	Calculated for $C_6H_2(C_6H_5NH)(NO_2)_2CH_2C(N_2HC_6H_5)CH_3$.	Found.
Nitrogen	17.28	16.97

Properties. — The hydrazone crystallizes well in reddish brown scales, resembling strongly in general appearance the officinal ferric citrate. The scales often reach a diameter of 3 to 4 millimeters. Under the microscope plates were observed which seemed to belong to the monoclinic system, but with these were very irregular forms, often serrated on one or both sides, or irregularly diamond-shaped with re-entering angles, usually either grouped in radiating masses, or in crowded branching collections of thick needles. It melts at 140°, but, as it seems to be slightly decomposed by crystallization, it was difficult to determine the melting point with perfect exactness. It is essentially insoluble in ligroine or cold water; very slightly soluble in boiling water or in ether; slightly soluble in cold alcohol, more soluble, but still not freely, in hot; more soluble in methyl than in ethyl alcohol; slightly soluble in cold glacial acetic acid, freely in hot; soluble in cold benzol or carbonic disulphide, freely soluble in these solvents when hot; easily soluble in chloroform or acetone, even in the cold. As the benzol solution deposits the substance in a viscous state, it is best to crystallize from a mixture of alcohol and benzol, as described above in speaking of its preparation. Strong hydrochloric acid has no action upon it. Strong nitric acid seems to decompose it, dissolving a little of the product. Strong sulphuric acid dissolves it with a yellowish brown color.

Neither sodic or ammonic hydrate, nor potassic carbonate, nor acid sodic carbonate, gives any action with it in aqueous solution, hot or cold, or even on addition of alcohol; but if it is warmed with sodic hydrate, water, and alcohol, a little dissolves with a brown color, and if a drop of sodic hydrate is added to an alcoholic solution, a dark brownish red solution is formed, which is decomposed by water. It may be, therefore, that the substance has not lost completely the power of forming salts, but it is on the whole more probable that the salt is derived from anilidodinitrobenzylmethylketone formed by the action of the sodic hydrate on the hydrazone, as the action was certainly accompanied by decomposition, since there was a smell of isocyanphenyl, and the hydrazone could not be recovered from the solution in sodic hydrate.

The study of the bromdinitrobenzylmethylketone will be continued in this laboratory.